

## COMPARISON OF LARGE AND ULTRA-SMALL $\Delta^{14}\text{C}$ MEASUREMENTS IN CORE TOP BENTHIC FORAMINIFERA FROM THE OKHOTSK SEA

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**ABSTRACT.** The radiocarbon activity of benthic foraminifera was investigated in surface sediments from a high deposition rate location at a depth of 1000 m in the Okhotsk Sea. Sediments were preserved and stained with Rose Bengal to identify foraminifera that contain cytoplasm. The benthic fauna at this site is dominated by large specimens of *Uvigerina peregrina*, and bulk samples (~150 individuals) of stained and unstained specimens were dated. The stained sample was about 240  $^{14}\text{C}$  yr younger than the unstained, and the presence of bomb  $^{14}\text{C}$  is inferred by comparison to water column data in the nearby open North Pacific. Using new methods, multiple measurements were also made on samples of three stained and unstained individuals (as small as 7  $\mu\text{g C}$ ). Results are consistent with those from the bulk samples. This suggests that similar ultra-small measurements could be made at other locations to reveal the age distribution of individuals in a sediment sample in order to assess the extent of bioturbation and the presence of bomb  $^{14}\text{C}$  contamination.

### INTRODUCTION

The mixing of marine sediments by burrowing animals, known as bioturbation, is a serious problem in extracting climate and paleocean data from sediments that underlie oxic bottom waters. Bioturbation has been modeled numerically (Berger and Heath 1968), and its effects are easily seen in sediment cores by the mottled appearance of different lithologies and by dispersal of volcanic ash shards or extraterrestrial particles from layers that were deposited in a geologic instant (e.g. Glass 1969). Bioturbation coupled with carbonate dissolution can severely bias radiocarbon ages in planktonic foraminifera (Barker et al. 2007). Biologists work around the bioturbation problem by staining (such as with Rose Bengal) or otherwise identifying living tissue. Whereas this works for core top sediments, it does not apply to paleostudies of pre-modern sediment. Accordingly, because there are relatively few sediment core locations where core top sediments were stained, and because the number of individuals that were living (or recently living) is small compared to the number of empty shells, most core top calibration studies use a mixture of old and young shells. This adds an unknown bias to such calibrations. The average age of this mixture depends on the accumulation rate of the sediment; for this reason (and others), paleoceanographers aim for core locations with high deposition rates.

Northeast Bermuda Rise is a classic location for high-resolution studies of paleoclimate and paleocean change because of its high deposition rate and because it is bathed by North Atlantic Deep Water. It was at this location that bomb  $^{14}\text{C}$  (fraction modern ( $F_m$ ) > 1) was first reported in core top planktonic foraminifera from the open sea (Keigwin 1996). Many subsequent studies of high-resolution paleochanges have also identified the bomb signal in core tops, and this is usually taken to mean that the core top is zero age and environmental conditions measured by proxies ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\text{Mg/Ca}$ , alkenone-based temperatures, for example) are representative of the overlying ocean.

This assumption was tested for  $^{14}\text{C}$  because that tracer is important for evaluating past changes in ocean ventilation (renewal of bottom waters) (Keigwin and Guilderson 2009). It is a particularly vexing problem because most locations in the ocean are contaminated by the bomb signal. Thus, it is difficult to calibrate the proxy, in this case the  $\Delta^{14}\text{C}$  of benthic foraminifera, because (1) benthic foraminifera are not often abundant enough for analysis in small core top samples, and (2) we do not know the distribution of  $^{14}\text{C}$  very well in the pre-bomb ocean. Keigwin and Guilderson (2009) concluded that even in core top planktonic foraminifera with  $F_m > 1$ , the benthic foraminifera are often too old because of bioturbation. They also concluded that the best hope for unmixing the core top  $^{14}\text{C}$  signal would be to measure  $^{14}\text{C}$  in individual foraminifera. Here, we report progress on that effort.

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## METHODS

We selected for study the top of a box core (BC) that was retrieved from Deryugen Basin, off northern Sakhalin Island in the Okhotsk Sea (53°32.7'N, 144°33.1'E, 1005 m water depth). BC32 was taken in September 1993 aboard voyage 25 of R/V *Akademik Alexander Nesmeyanov*, the same expedition that carried out World Ocean Circulation Experiment (WOCE) line P01W. A large volume of sediment was collected from the upper centimeter of BC32 by scooping the surface between subcore tubes. This sediment was stained with Rose Bengal and preserved in formalin at sea, and in the lab onshore the sediment was dried and washed over a 63- $\mu$ m sieve. Benthic and planktonic foraminifera were picked from the fraction >150  $\mu$ m. A stable isotope stratigraphy was developed for the planktonic foraminifera *Neoglobobulimina pachyderma* (left coiling) using the VG Prism mass spectrometer at the National Ocean Sciences Accelerator Mass Spectrometer Facility (NOSAMS) in Woods Hole, Massachusetts. Stained and unstained samples of the benthic foraminifer *Cibicides* were also analyzed for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  (Keigwin 1998).

The benthic foraminifer *Uvigerina peregrina* is a large, heavily calcified species that is very abundant in these samples. We made  $\Delta^{14}\text{C}$  measurements on ~200 (~2.4 mg) stained and unstained individuals using standard NOSAMS methods (Gagnon et al. 2000), and we experimented making measurements on samples that contained just three individuals (~70  $\mu\text{g CaCO}_3$ ). In order to minimize blank contributions associated with standard NOSAMS carbonate hydrolysis methods, a more novel approach utilizing the Prism II mass spectrometer (MS) was adopted to hydrolyze the individual tests. Vacuum quality in the Prism MS source is typically measured in the  $10^{-9}$  torr range, where standard vacuum quality in NOSAMS sample preparation laboratory (SPL) systems averages  $10^{-5}$  torr. The Prism II mass spectrometer is capable of measuring stable isotopic values ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) on carbonate samples containing as little as 10  $\mu\text{g CaCO}_3$ . We believed this would be the ideal platform for generating and capturing  $\text{CO}_2$  evolved from individual foraminifera based on system cleanliness, excellent vacuum quality, and low internal volumes, all significant factors in minimizing process-induced contamination. Five samples of three individual stained and unstained foraminifera were weighed into stainless steel boats (Table 1). Secondary standards (IAEA C-1 and IAEA C-2) were also weighed and added to the beginning, middle, and end of the reaction sequence. The boats were loaded into a 40-position VG Isocarb common acid bath system and run using standard procedures designed to measure  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of carbonates. Instead of allowing the evolved dry  $\text{CO}_2$  from each sample boat to enter the MS source, a small volume glass finger flask was installed and evacuated before the source inlet. The  $\text{CO}_2$  was cryogenically transferred to the finger flask and immediately installed on a NOSAMS SPL ultra-small graphite reactor. The ultra-small sample measurements and any associated machine and process blank corrections were made using the methods described in the companion manuscript by Shah Walter et al. (2015) in this issue.

Finally, we experimented to determine if the presence of the Rose Bengal stain could have influenced our results. We acid hydrolyzed two samples of the stain in its powder form, and quantified values of 40 and 50 nanomoles  $\text{CO}_2$  respectively, about 10% of what would be necessary for an ultra-small  $^{14}\text{C}$  analysis. In lieu of combining multiple hydrolyzed Rose Bengal samples, we prepared two samples for conventional AMS organic carbon combustion and found the Rose Bengal compound to have a radiocarbon  $F_m = 0$ .

## RESULTS AND DISCUSSION

Oxygen isotope stratigraphy of BC32 indicates a continuous decrease of as much as 0.5‰ in *N. pachyderma* from the bottom of the core at 45 cm to the top (Figure 1). The long-term average value of about 2.5‰ is the same as the Holocene in Nesmeyanov core 15 to the southeast on Academy

of Sciences (Akademia Nauk) Rise (Keigwin 1998). The top of BC32 has a conventional  $^{14}\text{C}$  age on *N. pachyderma* of  $430 \pm 35$  BP and a date near the bottom (41.5 cm) is  $2230 \pm 30$  BP (Table 1). Because  $\Delta R$  in Okhotsk Sea surface waters is  $578 \pm 50$  yr (Kuzmin et al. 2007), the core top age is about 550  $^{14}\text{C}$  yr younger than the expected pre-bomb age and probably reflects the presence of bomb-produced  $^{14}\text{C}$ . The calibrated age at 41.5 cm is about 1200 BP, so the rate of sedimentation assuming zero age at the top is 33 cm/kyr, about three times higher than Nesmeyanov core 15. In addition to the planktonic  $^{14}\text{C}$  and  $\delta^{18}\text{O}$  results, the core top *Cibicidoides*  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (Keigwin 1998) also indicate that BC32 has an unusually good record of the past 1000 yr, right up to today.

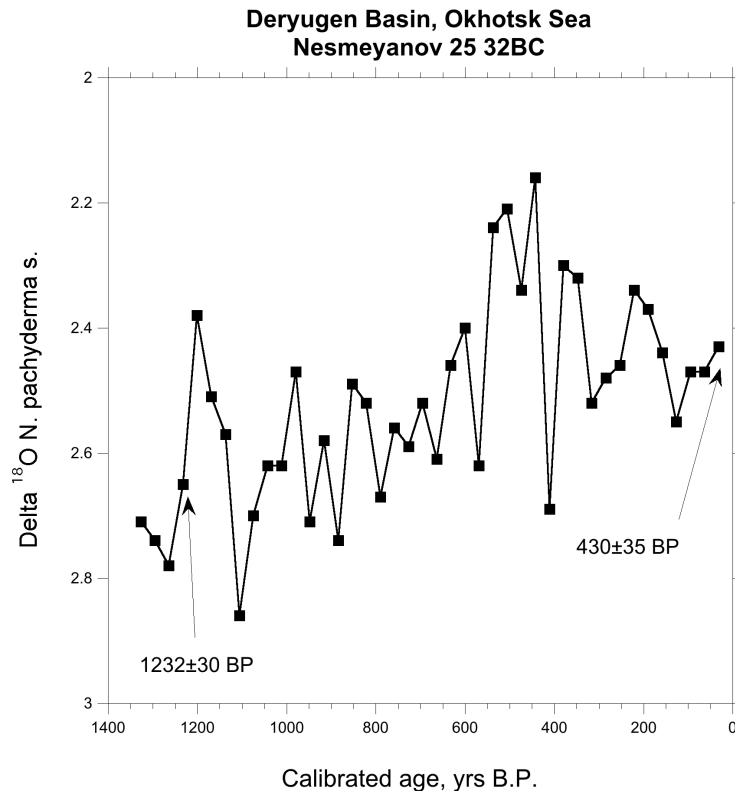


Figure 1 Stable isotope and planktonic  $^{14}\text{C}$  results on Nesmeyanov 25 BC32. The oxygen isotope series is typical of values observed elsewhere in the Okhotsk Sea, and the dates suggest high deposition rates of about 33 cm kyr $^{-1}$ . These and other data mark this location as ideal for experimenting with ultra-small  $^{14}\text{C}$  analyses of benthic foraminifera.

The abundance and size of *U. peregrina* made it possible to compare the  $^{14}\text{C}$  ages of stained and unstained specimens. In bulk samples of ~150 individuals, we found that the stained sample, as expected, is younger than the unstained sample, by about 240  $^{14}\text{C}$  yr (Table 1). Although there are no  $\Delta^{14}\text{C}$  data from Okhotsk Sea bottom waters near our core site at 1005 m, the  $\Delta^{14}\text{C}$  in the open subpolar North Pacific at 1000 m depth is about  $-200\text{‰}$ , with a minimum near the Okhotsk Sea of  $-210\text{‰}$  (Talley 2007). Our results on stained *U. peregrina* from Deryugen Basin ( $-177\text{‰}$ ) indicate higher  $\Delta^{14}\text{C}$ , probably reflecting the presence of bomb-produced  $^{14}\text{C}$ . This is possible because surface ocean freezing and brine rejection in the northern Okhotsk Sea create dense shelf waters. These undergo vertical mixing in the Kurile Island region and contribute to the ventilation of the subpolar

North Pacific (Talley 1991). The greater age of unstained specimens could mean that bioturbation introduced them to surface sediments from 5 to 10 cm below, but this seems unlikely considering the high sedimentation rate at this location. Alternatively, results on the unstained foraminifera could reflect the  $\Delta^{14}\text{C}$  of the pre-bomb ocean at this location. Judging from the WOCE line P13 data (<http://cdiac3.ornl.gov/waves/discrete/>), natural  $^{14}\text{C}$  (Rubin and Key 2002) at about 1000 m is 10 to 15‰ higher than measured  $\Delta^{14}\text{C}$ . Although this difference is small, it is consistent that the measured value in the bulk unstained *U. peregrina* (−202‰) is about 10‰ higher than the value on the Pacific side of the Kurile Islands.

Table 1 Radiocarbon results on the planktonic foraminifera *N. pachyderma* from the top and bottom of Nesmeyanov 25 BC32, and results on benthic foraminifera *U. peregrina* from the core top.

Sample	Accession #	Mass (µg C)	$^{14}\text{C}$ yr BP	Error	Fm	Fm error	$\Delta^{14}\text{C}$
<i>BC-32 N. pachyderma</i>							
0–1 cm	OS-14067	1080	430	35	0.9450	0.0044	−56.0
41.5 cm	OS-53167	500	2250	30	0.7560	0.0028	−249.0
<i>BC-32 U. peregrina</i>							
0–1 cm stained	OS-62197	256	1530	25	0.8269	0.0026	−177.4
0–1 cm unstained	OS-63273	245	1770	65	0.8023	0.0068	−201.9
Rose Bengal	OS-111940	1240	>49,710		0.0006	0.0015	
combustion	OS-111941	330	48,904	5320	0.0023	0.0015	
3 stained	OS-108337	11	1660	140	0.8135	0.0138	−190.7
<i>U. peregrina</i>	OS-108338	11	1440	130	0.8356	0.0136	−168.7
individuals	OS-108340	10	1430	170	0.8369	0.0175	−167.4
	OS-108344	9	1510	210	0.8284	0.0217	−176.0
	OS-108345	8	1490	200	0.8304	0.0212	−173.9
<b>Stained average =</b>			<b>1506</b>	<b>170</b>	<b>0.8289</b>	<b>0.0176</b>	<b>−175.3</b>
<b>1σ error =</b>			<b>92.4</b>	<b>35</b>	<b>0.0093</b>	<b>0.0039</b>	<b>9.3</b>
3 unstained	OS-108336	11	1930	140	0.7865	0.0139	−217.6
<i>U. peregrina</i>	OS-108339	11	2000	160	0.7792	0.0158	−224.8
individuals	OS-108341	10	1510	220	0.8283	0.0229	−176.0
	OS-108342	9	1740	180	0.8048	0.0181	−199.3
	OS-108346	7	1810	250	0.7979	0.0246	−206.3
<b>Unstained average =</b>			<b>1798</b>	<b>190</b>	<b>0.7993</b>	<b>0.0191</b>	<b>−204.8</b>
<b>1σ error =</b>			<b>190.2</b>	<b>45</b>	<b>0.0190</b>	<b>0.0046</b>	<b>18.9</b>

Measurements on ultra-small samples of three individual *U. peregrina* (Shah Walter et al. 2015) support results on the much larger (bulk) samples (Figure 2). The mean of five analyses on stained *U. peregrina* ( $1506 \pm 92$   $^{14}\text{C}$  yr) is within 1σ of the result on the bulk sample ( $1530 \pm 25$  BP), and the mean on unstained specimens ( $1798 \pm 190$   $^{14}\text{C}$  yr) is equal to the mean of the unstained bulk sample ( $1770 \pm 65$   $^{14}\text{C}$  yr). However, the scatter on unstained groups of three individuals is greater on the unstained samples by a factor of 2 (190 vs. 92  $^{14}\text{C}$  yr). This is clearly the result of bioturbation. Whereas the bulk analysis on specimens that took the Rose Bengal stain has a 1σ error of only 25 yr, it must be emphasized that this only means that there was cytoplasm in the shell and not that the animal was alive at the time of collection (Bernhard et al. 2006). It is not known how long

cytoplasm will survive in a shell in the surface mixed layer on the seafloor, but the analytical error is small and for our purposes these individuals were alive or recently alive at the time of collection.

### Sea of Okhotsk Coretop Benthic Foraminifera

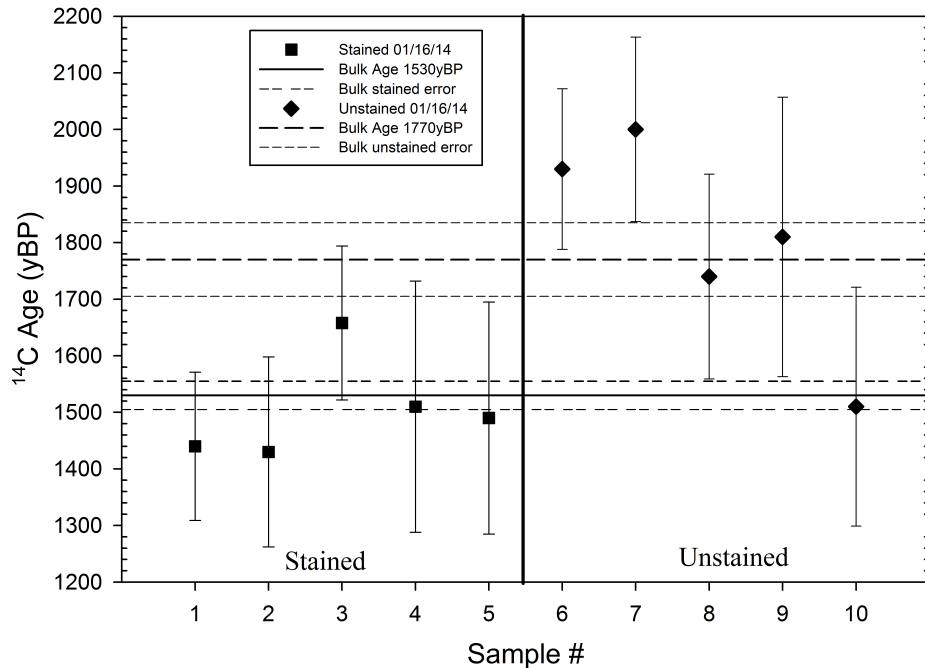


Figure 2 Radiocarbon results on core top *Uvigerina peregrina* from Nesmeyanov 25 BC32. Horizontal lines and error bars show results on shells that were Rose Bengal stained (cytoplasm-containing) samples of ~150 shells (lower line), and results on a similar number of shells that did not stain (upper line). Individually plotted data are results on stained (squares) and unstained (diamonds) samples of three shells of *U. peregrina*. Although the measurements on three shells have much larger errors than those on the bulk samples, the means are similar between large and ultra-small samples. Larger scatter in the small unstained samples than the small stained samples illustrates the effect of bioturbation on the age distribution of shells in a seafloor sample.

### CONCLUSIONS

Results from a high-deposition rate location in the Okhotsk Sea show that newly developed ultra-small  $^{14}\text{C}$  methods can distinguish between Rose Bengal stained (living or recently living) and unstained (dead) benthic foraminifera. Measurements on bulk samples that contain ~150 individuals, and the ultra-small measurements, based on three individual *U. peregrina*, give similar results. The stained foraminifera are on average more than 200  $^{14}\text{C}$  yr younger than those that did not stain, and their  $\Delta^{14}\text{C}$  is consistent with the presence of bomb-produced  $^{14}\text{C}$ . Similar experiments on unstained sediments from locations with lower deposition rates could be used to assess the extent of bioturbation and infer the distribution of  $\Delta^{14}\text{C}$  within the benthic foraminiferal population. Where deposition rates are high, similar experiments may also provide a new way to infer natural  $^{14}\text{C}$  values.

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